



VERIFICATION

The undersigned, of the below address, hereby certifies that he/she well knows both the English and Japanese languages, and that the attached is an accurate English translation of the Japanese Patent application filed on March 4, 2004 under No. P2004-060581.

The undersigned declares further that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 4th day of July, 2008.

Signature:

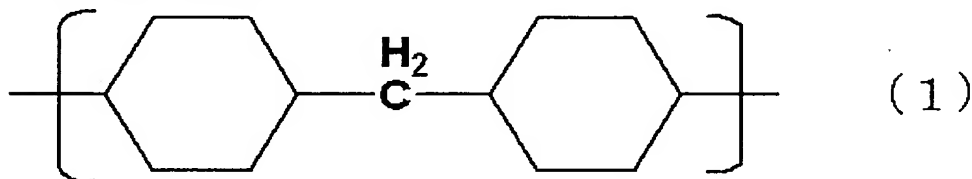

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Japan

[Document Name] Claims

[Claim 1] A prepreg obtained by impregnating a resin composition comprising a resin having a structure represented by the following general formula (1) into a fiber base material.

[Chemical Formula 1]



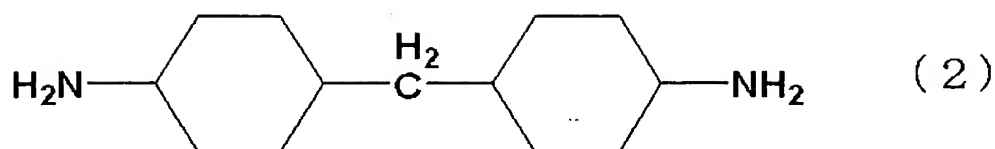
[Claim 2] A prepreg according to claim 1, wherein said resin composition is a resin composition comprising a thermosetting resin.

[Claim 3] A prepreg according to claim 1 or 2, wherein said thermosetting resin is an epoxy resin.

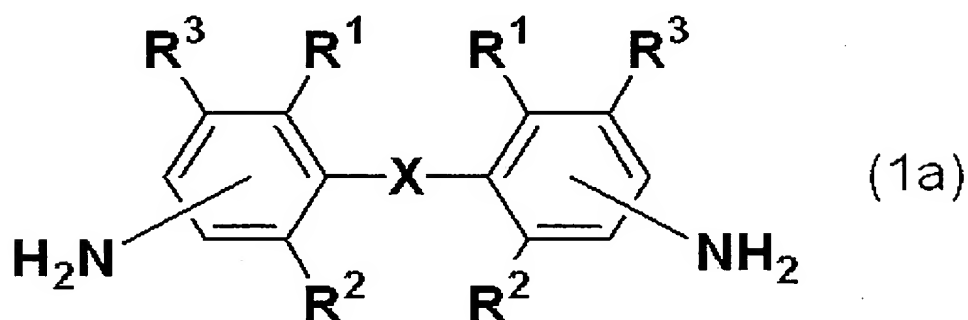
[Claim 4] A prepreg according to any one of claims 1 to 3, wherein said resin having a structure represented by the general formula (1) is a polyamideimide resin.

[Claim 5] A prepreg according to any one of claims 1 to 4, wherein said resin having a structure represented by the general formula (1) is a polyamideimide resin obtained by reacting a diisocyanate compound with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a diamine represented by the following general formula (2), a diamine with two or more aromatic rings represented by the following general formula (1a) or (1b), with trimellitic anhydride.

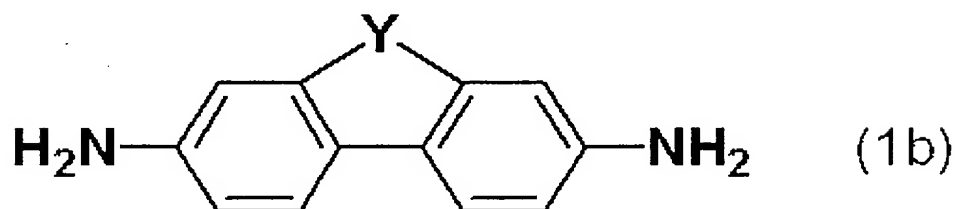
[Chemical Formula 2]



[Chemical Formula 3]

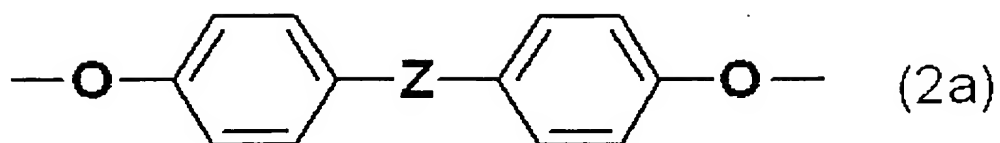


[Chemical Formula 4]

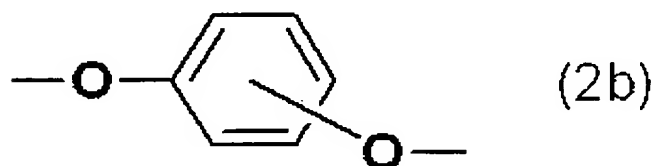


(wherein X represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, a single bond, a divalent group represented by the following general formula (2a) or a divalent group represented by the following general formula (2b), Y represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, and R¹, R² and R³ each independently or identically represent hydrogen, hydroxyl, methoxy, methyl or halogenated methyl.

[Chemical Formula 5]



[Chemical Formula 6]



wherein Z represents a C1-3 aliphatic hydrocarbon group, C1-3
 5 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group,
 carbonyl group, or a single bond.)

[Claim 6] A prepreg according to any one of claims 1 to 5, wherein
 said epoxy resin is an epoxy resin with two or more glycidyl groups.

[Claim 7] A prepreg according to any one of claims 1 to 6, wherein
 10 the thickness of said fiber base material is 5-50 μm .

[Claim 8] A metal foil-clad laminate obtained by stacking a prescribed
 number of preregs according to any one of claims 1 to 7, situating a
 metal foil on either or both sides thereof and subjecting the stack to
 heat and pressure.

15 [Claim 9] A printed circuit board obtained by forming a circuit on said
 metal foil-clad laminate according to claim 8.

[Document Name] Specification

[Title of the Invention] PREPREG, METAL CLAD LAMINATE,
AND PRINTED CIRCUIT BOARD USING SAME

[Field of the Invention]

5 [0001]

The present invention relates to a prepreg and to a metal foil-clad laminate and printed circuit board that employ it.

[Prior Art]

10 [0002] Laminates for printed circuit boards are formed by stacking a prescribed number of prepregs comprising an electrical insulating resin composition as the matrix, and subjecting them to heat and pressure for integration.

15 Metal-clad laminates are used for formation of printed circuits by a subtractive process. Metal-clad laminates are fabricated by stacking a metal foil such as copper foil on a surface (either or both surfaces) of a prepreg and subjecting the stack to heat and pressure. As electrical insulating resins there are commonly used thermosetting resins such as phenol resins, epoxy resins, polyimide resins, bismaleimide-triazine resins and the like. Thermoplastic resins such as fluorine resins or
20 polyphenylene ether resins are also sometimes used.

 [0003] On the other hand, with the increasing popularity of data terminal devices such as personal computers and cellular phones there is a trend toward miniaturization and high-densification of the printed circuit boards mounted therein. The mounting methods are
25 advancing from pin-insertion types to surface-mounted types, and also to area array types of which BGA (ball grid arrays) using plastic boards

are a typical example. In boards where bare chips such as BGA are directly mounted, connection between the chips and boards is commonly achieved by wire bonding using thermosonic bonding. In such cases, the board on which the bare chip is mounted is exposed to high temperatures of 150°C and above, and therefore the electrical insulating resin must have some degree of heat resistance.

[0004] As lead-free solders become more common for environmental reasons, the melting points of solders are increasing as a result. Thus, even higher heat resistance is demanded for boards. Demand for halogen-free materials is also increasing, thus precluding the use of bromine-based flame retardants.

[0005] Moreover, the "repair properties" allowing mounted chips to be removed are often required. During repair, the boards are subjected to about the same level of heating as during chip mounting, after which further heat treatment is carried out for remounting of chips. Such treatment has often resulted in peeling between the fiber material and resin in conventional insulating resin systems. Thus, boards exhibiting repair properties must also have cycling heat shock-resistant properties at high temperatures.

[0006] Prepregs have been proposed that exhibit excellent heat shock resistance, reflow resistance and crack resistance, and improved microwiring formation properties, by impregnating a resin composition comprising a polyamideimide as an essential component into the fiber material (see Patent Literature 1).

[0007] Also, with the trend toward greater miniaturization and higher performance of electronic devices, it is becoming

necessary to house part-mounted printed circuit boards in increasingly limited spaces. This is accomplished by methods of arranging multiple printed circuit boards in stacks and connecting them alternately with wire harnesses or flexible wiring boards. There are
5 also used rigid-flex boards which are layered combinations of polyimide-based flexible boards and conventional rigid boards.

[Patent Literature 1] Japanese Unexamined Patent Publication No. 2003-55486

[Disclosure of the Invention]

10 [Problem to be Solved by the Invention]

[0008] The present invention solves the problems of the prior art described above, and is to provide a printed circuit board with excellent dimensional stability and heat resistance and the ability to be bent and housed at high density in electronic device packages, by
15 impregnating a thin fiber base material with a resin having excellent adhesion with metal foils or fiber base materials, excellent heat resistance and high pliability, as well as to provide a prepreg and metal foil-clad laminate which yield said printed circuit board.

[Means for Solving the Problem]

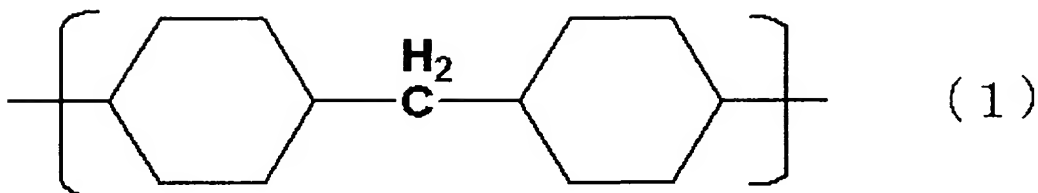
20 [0009]

The present invention relates to the following.

(1) A prepreg obtained by impregnating a resin composition comprising a resin having a structure represented by the following general formula (1) into a fiber base material.

25 [0010]

[Chemical Formula 1]



(2) A prepreg according to (1), wherein said resin composition is a resin composition comprising a thermosetting resin.

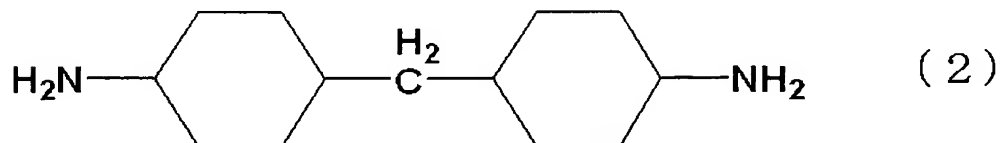
(3) A prepreg according to (1) or (2), wherein said thermosetting resin is an epoxy resin.

(4) A prepreg according to any one of (1) to (3), wherein said resin having a structure represented by the general formula (1) is a polyamideimide resin.

(5) A prepreg according to any one of (1) to (4), wherein said resin having a structure represented by the general formula (1) is a polyamideimide resin obtained by reacting a diisocyanate compound with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a diamine represented by the following general formula (2), a diamine with two or more aromatic rings represented by the following general formula (1a) or (1b), with trimellitic anhydride.

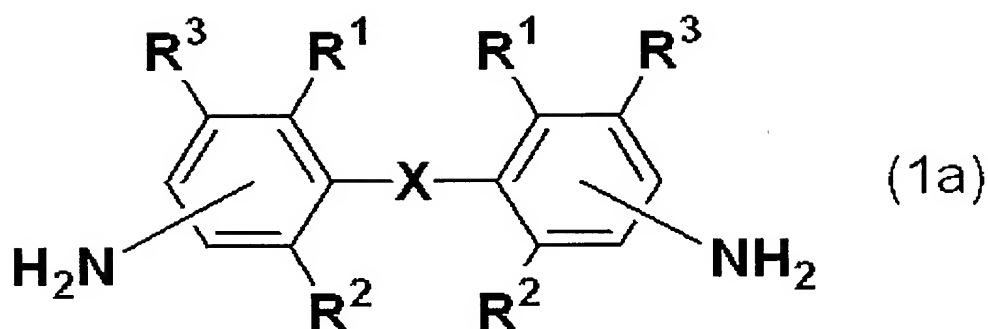
[0011]

[Chemical Formula 2]



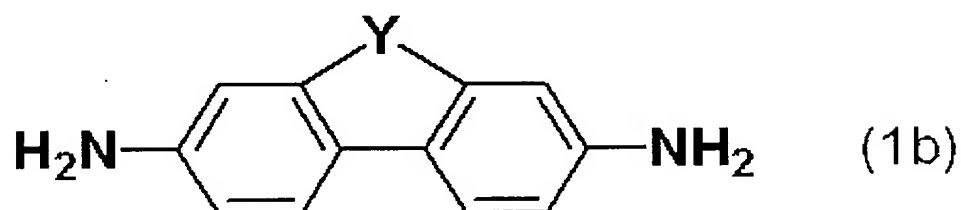
[0012]

[Chemical Formula 3]



[0013]

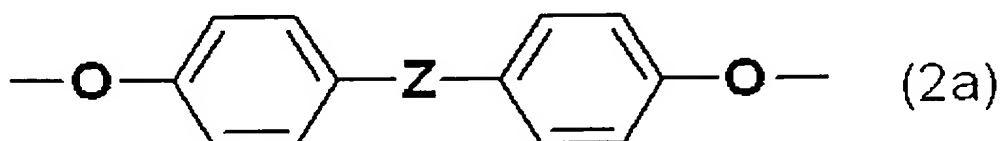
[Chemical Formula 4]



(wherein X represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, a single bond, a divalent group represented by the following general formula (2a) or a divalent group represented by the following general formula (2b), Y represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, and R¹, R² and R³ each independently or identically represent hydrogen, hydroxyl, methoxy, methyl or halogenated methyl.

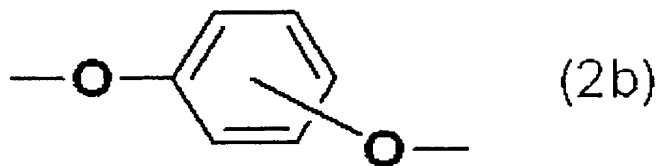
[0014]

[Chemical Formula 5]



[0015]

[Chemical Formula 6]



wherein Z represents a C1-3 aliphatic hydrocarbon group, C1-3
 5 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group,
 carbonyl group, or a single bond.)

(6) A prepreg according to (3) or (4), wherein said epoxy resin is an
 epoxy resin with two or more glycidyl groups.

(7) A prepreg according to any one of (1) to (5), wherein the thickness
 10 of said fiber base material is 5-50 μm .

(8) A metal foil-clad laminate obtained by stacking a prescribed
 number of prepregs according to any one of (1) to (7), situating a
 metal foil on either or both sides thereof and subjecting the stack to
 heat and pressure.

15 (9) A printed circuit board obtained by forming a circuit on said metal
 foil-clad laminate according to (8).

[Effects of the Invention]

[0016]

20 The metal foil-clad laminate and the printed circuit board obtained by
 using the prepreg of the present invention have the ability to be bent
 and have excellent dimensional stability, heat resistance and PCT
 resistance. This prepreg can be housed at high density in electronic
 device packages because of the ability to be bent arbitrarily when
 manufacturing the printed circuit board.

[Best Mode for Carrying Out the Invention]

[0017]

The prepreg of the present invention is the prepreg obtained by impregnating a resin composition comprising a resin having a structure represented by the preceding general formula (1) into a fiber base material. The resin having a structure represented by the preceding general formula (1) is used in the present invention. As the resin having a structure represented by the general formula (1) there may be mentioned polyimide resins, polyamideimide resins and maleimide resins, but it is not limited to these.

[0018]

An polyimide resins can be obtained by reacting a diamine represented by the general formula (2) with tetracarboxylic acid dianhydrides at equal molar ratio to form a polyamic Acid represented by the general formula (1) and then proceeding anhydration and ring-closing reaction. In this case, it is preferred that total mole amount of the diamine represented by the general formula (2) and the other diamine is equimolar to the tetracarboxylic acid dianhydrides.

[0019]

As maleimide resins there may be used those obtained by reacting a diamine compound and maleic anhydride at a molar ratio of 1:2 to form a bismaleimide, and then mixing this with a triazine or another thermosetting resin.

[0020]

The polyamideimide resin having a structure represented by the general formula (1) is especially preferred in the present invention. A

polyamideimide resin having a structure represented by the general formula (1) obtained by reacting a diisocyanate compound with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a diamine represented by the general formula (2),
 5 a diamine with two or more aromatic rings represented by the following general formula (1a) or (1b), with trimellitic anhydride is especially preferred.

[0021]

For synthesis of the polyamideimide resin having a structure represented by the general formula (1), the blending ratio of the
 10 diamine represented by the general formula (2) with a total mole b of the diamine two or more aromatic rings and the siloxanediamine is preferably $a/b = 0.1/99.9-99.9/0.1$ (molar ratio), more preferably $a/b = 10/90-50/50$ and even more preferably $a/b = 20/80-40/60$. Example for
 15 the diamine represented by the general formula (2) includes WONDAMINE (trade name of New Japan Chemical Co., Ltd.).

[0022]

Examples of aromatic diamines with two or more aromatic rings represented by the general formula (1a) or (1b) (aromatic diamines)
 20 include 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), bis[4-(3-aminophenoxy)phenyl]sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, bis[4-(4-aminophenoxy)phenyl]methane, 4,4'-bis(4-aminophenoxy)biphenyl,
 25 bis[4-(4-aminophenoxy)phenyl]ether, bis[4-(4-aminophenoxy)phenyl]ketone, 1,3-bis(4-aminophenoxy)benzene, 1,4-

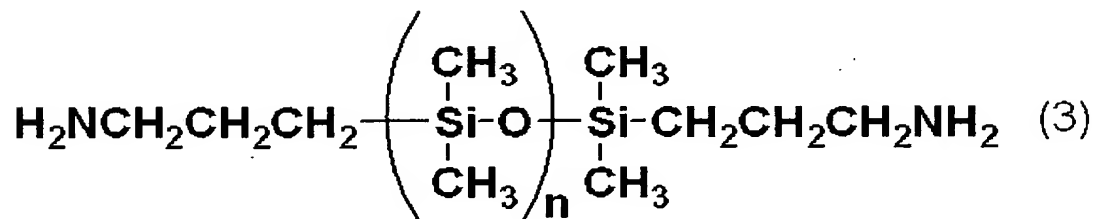
bis(4-aminophenoxy)benzene, 2,2'-dimethylbiphenyl-4,4'-diamine,
 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine, 2,6,2',6'-tetramethyl-
 4,4'-diamine, 5,5'-dimethyl-2,2'-sulfonyl-biphenyl-4,4'-diamine, 3,3'-
 dihydroxybiphenyl-4,4'-diamine, (4,4'-diamino)diphenyl ether, (4,4'-
 5 diamino)diphenylsulfone, (4,4'-diamino)benzophenone, (3,3'-
 diamino)benzophenone, (4,4'-diamino)diphenylmethane, (4,4'-
 diamino)diphenyl ether and 3,3'-diaminodiphenyl ether.

[0023]

As siloxanediamines used in present invention there may be
 10 mentioned compounds represented by the following general formulas
 (3)-(6).

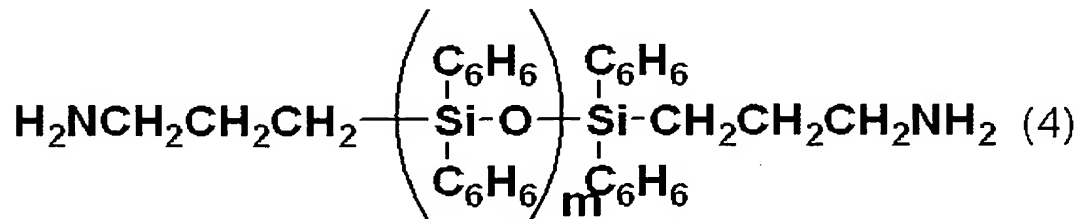
[0024]

[Chemical Formula 7]



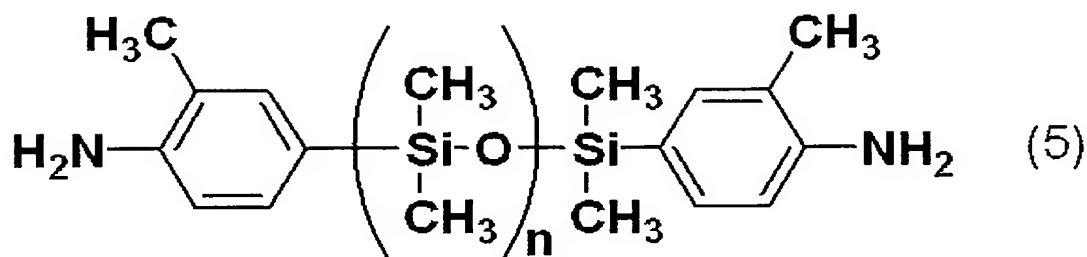
[0025]

[Chemical Formula 8]



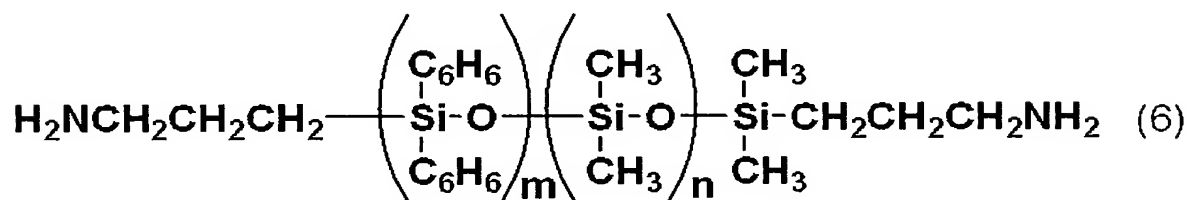
[0026]

[Chemical Formula 9]



[0027]

[Chemical Formula 10] ...



5

[0028]

10

Examples of siloxanediamines represented by general formula (3) above include X-22-161AS (450 amine equivalents), X-22-161A (840 amine equivalents), X-22-161B (1500 amine equivalents) (all products of Shin-Etsu Chemical Co., Ltd.), BY16-853 (650 amine equivalents) and BY16-853B (2200 amine equivalents) (all products of Dow Corning Toray Silicone Co., Ltd.). Examples of siloxanediamines represented by general formula (6) above include X-22-9409 (700 amine equivalents) and X-22-1660B-3 (2200 amine equivalents) (both products of Shin-Etsu Chemical Co., Ltd.).

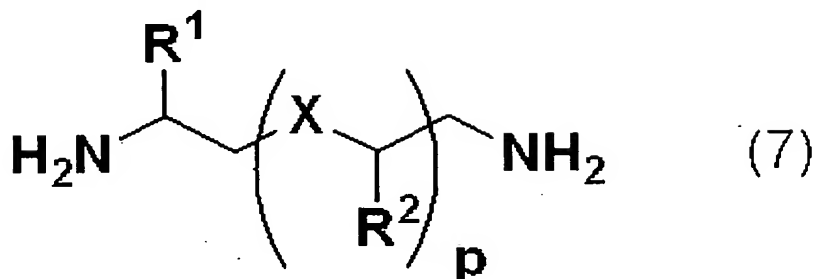
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[0029]

There may also be used an aliphatic diamine in addition to the diamine represented by the general formula (2). Examples of such aliphatic diamines include compounds represented by the following general formula (7).

[0030]

[Chemical Formula 11]



[In formula, X represents methylene, sulfonyl, ether, carbonyl or a single bond, R¹ and R² each represent hydrogen, alkyl, phenyl or substituted phenyl, and p represents an integer of 1-50.]

[0031]

As specific examples of R¹ and R² there are preferred hydrogen, C1-3 alkyl, phenyl and substituted phenyl, and examples of substituents bonded to phenyl include C1-3 alkyl, halogens and the like.

[0032]

From the standpoint of achieving both a low elastic modulus and high T_g, the aliphatic diamine is preferably one wherein X in general formula (7) above is an ether group. Examples of such aliphatic diamines include JEFFAMINE D-400 (San Techno Chemical Co., Ltd., 400 amine equivalents) and JEFFAMINE D-2000 (San Techno Chemical Co., Ltd., 1000 amine equivalents).

[0033]

As diisocyanate compounds to be used for production of polyamideimide resins having a structure represented by the general formula (1) in the present invention there may be mentioned compounds represented by the following general formula (8).

[0034]

[Chemical Formula 12]



[0035]

5 In formula, D is a divalent organic group with at least one aromatic ring, or a divalent aliphatic hydrocarbon group, and it is preferably at least one group selected from the group consisting of $-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$, tolylene, naphthylene, hexamethylene, 2,2,4-trimethylhexamethylene and isophorone.

10 [0036]

As diisocyanate compounds represented by general formula (8) above there may be used aliphatic diisocyanate or aromatic diisocyanate compounds, but aromatic diisocyanate compounds are preferred, and combinations of both are especially preferred.

15 [0037]

Examples of aromatic diisocyanate compounds include 4,4'-diphenylmethanediisocyanate (MDI), 2,4-tolylenediisocyanate, 2,6-tolylenediisocyanate, naphthalene-1,5-diisocyanate, 2,4-tolylene dimer and the like, with MDI being particularly preferred. Using
20 MDI as an aromatic diisocyanate can improve the flexibility of the obtained polyamideimide resin.

[0038]

Examples of aliphatic diisocyanate compounds include hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene
25 diisocyanate and isophorone diisocyanate.

[0039]

When an aromatic diisocyanate and aliphatic diisocyanate are used in combination, the aliphatic diisocyanate is preferably added at about 5-10 mol% with respect to the aromatic diisocyanate. Such use in combination can further improve the heat resistance of the obtained polyamideimide resin.

[0040]

As thermosetting resins to be used for the invention there may be mentioned epoxy resins, polyimide resins, unsaturated polyester resins, polyurethane resins, bismaleimide resins, triazine-bismaleimide resins and phenol resins. The thermosetting resin is preferably used at 1-200 parts by weight with respect to 100 parts by weight of the polyimide resin. In the present invention, there are preferred a thermosetting resin having organic groups that can react with the amide groups of the polyamideimide resin, more preferred a glycidyl group-containing epoxy resins. The thermosetting resin is used at 1-200 parts by weight with respect to 100 parts by weight of the polyamideimide resin in the present invention, if the content of the thermosetting resin is less than 1 part by weight, the solvent resistance will tend to be inferior, if it exceeds 200 parts by weight, the T_g will be lower due to the unreacted thermosetting resin, leading to insufficient heat resistance and undesirable reduction in flexibility. Thus, the content of the thermosetting resin is more preferably 3-100 parts by weight and even more preferably 10-60 parts by weight to 100 parts by weight of the polyamideimide resin.

[0040]

As epoxy resins there may be mentioned polyglycidyl ethers obtained by reacting epichlorhydrin with a polyhydric phenol such as bisphenol A, a novolac-type phenol resin or an orthocresol/novolac-type phenol resin or with a polyhydric alcohol such as 1,4-buthane diol, polyglycidyl esters obtained by reacting epichlorhydrin with a polybasic acid such as phthalic acid or hexahydrophthalic acid, N-glycidyl derivatives of compounds with amine, amide or heterocyclic nitrogenous bases, and alicyclic epoxy resins.

[0042]

By using an epoxy resin as the thermosetting resin in the present invention, it is possible to cure at a temperature of below 180°C, and to further improve the thermal, mechanical and electrical properties by reacting with amide groups of the polyamideimide resin. It is preferred to use as the epoxy resin a combination of an epoxy resin with two or more glycidyl groups and its curing agent, a combination of an epoxy resin with two or more glycidyl groups and its curing accelerator, or a combination of an epoxy resin with two or more glycidyl groups and its curing agent and curing accelerator. A greater number of glycidyl groups is preferred, with 3 or more being more preferred. The content of the thermosetting resin will differ depending on the number of glycidyl groups, and the content may be lower with a larger number of glycidyl groups.

[0043]

The curing agent and curing accelerator for the epoxy resin are not particularly restricted so long as they react with the epoxy resin or promote its curing, and there may be used, for example, amines,

imidazoles, polyfunctional phenols, acid anhydrides and the like. As amines there may be used dicyandiamide, diaminodiphenylmethane, guanylurea and the like. As polyfunctional phenols there may be used hydroquinone, resorcinol, bisphenol A and their halogenated forms, as well as novolac-type phenol resins and resol-type phenol resins that are condensates with formaldehyde. As acid anhydrides there may be used phthalic anhydride, benzophenonetetracarboxylic dianhydride, methylhymic acid and the like. As curing accelerators there may be used imidazoles such as alkyl-substituted imidazoles and benzimidazoles.

[0044]

The preferred amount of such a curing agent or curing accelerator is, in the case of an amine, an amount such that the equivalents of active hydrogen of the amine and epoxy equivalents of the epoxy resin are approximately equal. For an imidazole as the curing accelerator there is no simple equivalent ratio with active hydrogen, and the required amount is 0.001-10 parts by weight to 100 parts by weight of the epoxy resin. In the case of a polyfunctional phenol or acid anhydride, the required amount is 0.6-1.2 equivalents of phenolic hydroxyl or carboxyl groups with respect to one equivalent of the epoxy resin. A small amount of such a curing agent or curing accelerator will leave some amount of uncured epoxy resin and will lower the T_g (glass transition temperature), while a large amount will leave some amount of unreacted curing agent and curing accelerator, thereby lowering the insulating property. Since the epoxy equivalents of the epoxy resin

can also react with the amide groups of the polyamideimide resin, this is preferably taken into account.

[0045]

The prepreg can be obtained by preparing a varnish by mixing, dissolving and dispersing a resin composition for prepreg in an organic solvent, and then impregnating it into a fiber material and drying in the present invention. The organic solvent is not particularly restricted so long as it is able to dissolve the resin composition, and as examples there may be mentioned dimethylacetamide, dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone, γ -butyrolactone, sulfolane and cyclohexanone.

[0046]

The resin composition for prepreg is preferably the resin composition containing 100 parts by weight of a polyimide resin having a structure represented by the general formula (1) and 1-200 parts by weight of a thermosetting resin. This will increase the vaporization rate of the varnish solvent of the resin composition, making it possible to achieve a residual solvent content of 5 wt% or less even at a low temperature of below 150°C at which the thermosetting resin curing reaction is not promoted. As a result, the heat resistance adhesive seal have satisfactory adhesion between the fiber base material and copper foil.

[0047]

The prepreg can be fabricated by impregnating the fiber base material with the resin composition varnish and drying it in a temperature range of 80-180°C. The fiber base material is not particularly restricted so long as it is one used for fabrication of metal foil-clad

laminates and multilayer printed circuit boards, and there may be mentioned fiber base materials such as woven fabrics and nonwoven fabrics. As materials for the fiber base material there may be mentioned inorganic fibers such as glass, alumina, asbestos, boron, silica-alumina glass, silica glass, tirano, silicon carbide, silicon nitride and zirconia, organic fibers such as aramid, polyetherether ketone, polyetherimide, polyethersulfone, carbon and cellulose, and blended systems thereof, among which woven fabrics of glass fibers are preferred. Among these, glass cloths with a thickness of 5-50 μm are preferred as fiber base materials to be used in prepregs. By using a glass cloth with a thickness of 5-50 μm and using the resin composition of the present invention, it is possible to obtain a printed circuit board that can be folded as desired, and which undergoes minimal dimensional change with the temperature and humidity of the manufacturing process.

[0048]

The manufacturing conditions for the prepreg are not particularly restricted, but preferred are conditions wherein at least 80 wt% of the solvent used in the varnish evaporates. The fabrication process and drying conditions are also not particularly restricted, and for example, the temperature for drying may be 80-180°C, and the time may be adjusted in balance with the varnish gelling time. The impregnating amount of varnish is preferably such for a varnish solid content of 30-80 wt% with respect to the total amount of solid varnish and fiber base material.

[0049]

The manufacturing methods of insulating boards, laminates and metal foil-clad laminates are as follows. The prepreg of the present invention may be used alone or a plurality thereof laminated into a laminate, stacked with a metal foil on either or both sides as necessary, and subjected to hot pressure molding at a temperature in the range of 150-280°C or preferably 180-250°C, and a pressure in the range of 0.5-20 MPa or preferably 1-8 MPa, to fabricate an insulating board, laminate or metal foil-clad laminate. Using a metal foil to obtain metal foil-clad laminate, a printed circuit board can be obtained by forming a circuit to it.

[0050]

The metal foils used in the present invention include copper foils and aluminum foils, these metal foils having thicknesses of 5-200 μm which are generally used to laminate can be applied. The metal foil may be a composite foil with a three-layer structure provided with an interlayer made of nickel, nickel-phosphorus, nickel-tin alloy, nickel-iron alloy, lead, lead-tin alloy or the like, having a 0.5-15 μm copper layer and a 10-300 μm copper layer on either side, or a composite foil with a two-layer structure comprising aluminum and copper foils.

[Examples]

[0051]

The present invention will now be explained in greater detail by examples, with the understanding that the invention is in no way limited to these examples.

(Synthesis Example 1)

In a 1-liter separable flask equipped with a cock-stoppered 25-ml water measuring receptacle connected to a reflux condenser, and a thermometer and stirrer, there were charged 14.9 g (0.06 mol) of DDS (diaminodiphenylsulfone) as a diamine with two or more aromatic rings, 43.0 g (0.05 mol) of the reactive silicone oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 430) as a siloxanediamine, 72.0 g (0.36 mol) of JEFFAMINE D2000 (trade name of San Techno Chemical Co., Ltd., amine equivalents: 1000) as an aliphatic diamine, 11.3 g (0.054 mol) of WONDAMINE (trade name of New Japan Chemical Co., Ltd.) as a diamine represented by general formula (2) and 80.7 g (0.42 mol) of TMA (trimellitic anhydride), with 589 g of NMP (N-methyl-2-pyrrolidone) as an aprotic polar solvent, and the mixture was stirred at 80°C for 30 minutes. Next, 150 ml of toluene was loaded as an aromatic hydrocarbon for azeotropic distillation with water, and the temperature was raised for 2 hours of reflux at about 160°C. When approximately 7.2 ml of water had accumulated in the water measuring receptacle, cessation of water distillation was confirmed, and the temperature was raised to about 190°C for removal of the toluene while removing the distillate accumulated in the water measuring receptacle. Next, the solution was returned to room temperature (25°C), and 55.1 g (0.22 mol) of MDI (4,4'-diphenylmethanediisocyanate) was loaded as an aromatic diisocyanate for 2 hours of reaction at 190°C. Upon completion of the reaction there was obtained an NMP solution containing a polyamideimide resin.

[0052]

(Synthesis Example 2)

In a 1-liter separable flask equipped with a cock-stoppered 25-ml water measuring receptacle connected to a reflux condenser, and a thermometer and stirrer, there were charged 14.9 g (0.06 mol) of DDS (diaminodiphenylsulfone) as a diamine with two or more aromatic rings, 51.6 g (0.06 mol) of the reactive silicone oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 430) as a siloxanediamine, 52.0 g (0.26 mol) of JEFFAMINE D2000 (trade name of San Techno Chemical Co., Ltd., amine equivalents: 1000) as an aliphatic diamine, 11.3 g (0.054 mol) of WONDAMINE (trade name of New Japan Chemical Co., Ltd.) as a diamine represented by general formula (2) and 80.7 g (0.42 mol) of TMA (trimellitic anhydride), with 575 g of NMP (N-methyl-2-pyrrolidone) as an aprotic polar solvent, and the mixture was stirred at 80°C for 30 minutes. Next, 150 ml of toluene was loaded as an aromatic hydrocarbon for azeotropic distillation with water, and the temperature was raised for 2 hours of reflux at about 160°C. When approximately 7.2 ml of water had accumulated in the water measuring receptacle, cessation of water distillation was confirmed, and the temperature was raised to about 190°C for removal of the toluene while removing the distillate accumulated in the water measuring receptacle. Next, the solution was returned to room temperature (25°C), and 55.1 g (0.22 mol) of MDI (4,4'-diphenylmethanediisocyanate) was loaded as an aromatic diisocyanate for 2 hours of reaction at 190°C. Upon completion of the reaction there was obtained an NMP solution containing a polyamideimide resin.

[0053]

(Synthesis Example 3)

In a 1-liter separable flask equipped with a cock-stoppered 25-ml water measuring receptacle connected to a reflux condenser, and a thermometer and stirrer, there were charged 14.9 g (0.06 mol) of DDS (diaminodiphenylsulfone) as a diamine with two or more aromatic rings, 43.0 g (0.05 mol) of the reactive silicone oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 430) as a siloxanediamine, 72.0 g (0.36 mol) of JEFFAMINE D2000 (trade name of San Techno Chemical Co., Ltd., amine equivalents: 1000) as an aliphatic diamine, 11.3 g (0.054 mol) of WONDAMINE (trade name of New Japan Chemical Co., Ltd.) as a diamine represented by general formula (2) and 80.7 g (0.42 mol) of TMA (trimellitic anhydride), with 599 g of NMP (N-methyl-2-pyrrolidone) as an aprotic polar solvent, and the mixture was stirred at 80°C for 30 minutes. Next, 150 ml of toluene was loaded as an aromatic hydrocarbon for azeotropic distillation with water, and the temperature was raised for 2 hours of reflux at about 160°C. When approximately 7.2 ml of water had accumulated in the water measuring receptacle, cessation of water distillation was confirmed, and the temperature was raised to about 190°C for removal of the toluene while removing the distillate accumulated in the water measuring receptacle. Next, the solution was returned to room temperature (25°C), and 60.1 g (0.24 mol) of MDI (4,4'-diphenylmethanediisocyanate) was loaded as an aromatic diisocyanate for 2 hours of reaction at 190°C. Upon completion of the

reaction there was obtained an NMP solution containing a polyamideimide resin.

[0054]

(Example 1)

5 After mixing 250.0 g of an NMP solution of the polyamideimide resin (PAI) of Synthesis Example 1 (32 wt% solid resin content), 40.0 g of NC3000 (trade name of Nippon Kayaku Co., Ltd.) as an epoxy resin (Ep) (dimethylacetamide solution with 50 wt% solid resin content) and
10 0.2 g of 2-ethyl-4-methylimidazole, the mixture was stirred for about 1 hour until uniformity of the resin and then allowed to stand for 24 hours at room temperature (25°C) for defoaming to obtain a resin composition varnish.

[0055]

(Example 2)

15 A resin composition varnish was obtained in the same manner as Example 1, except that an NMP solution of the polyamideimide resin (PAI) of Synthesis Example 2 was used instead of the polyamideimide resin (PAI) of Synthesis Example 1.

[0056]

20 (Example 3)

A resin composition varnish was obtained in the same manner as Example 1, except that an NMP solution of the polyamideimide resin (PAI) of Synthesis Example 3 was used instead of the polyamideimide resin (PAI) of Synthesis Example 1.

25 [0057]

(Comparative Example 1)

A resin composition varnish was obtained in the same manner as Example 1, except that an NMP solution of KS6600 (trade name of Hitachi Chemical Co., Ltd.) as a polyamideimide resin (PAI) without the structure of general formula (1) was used instead of the polyamideimide resin (PAI) of Synthesis Example 1.

[0058]

(Fabrication of prepreg and metal foil-clad laminate)

The resin composition varnishes prepared in Examples 1-3 and Comparative Example 1 were each impregnated into a 0.028 mm-thick glass cloth (trade name: 1037 by Asahi Shwebel Co., Ltd.), and then heated at 150°C for 15 minutes for drying to obtain a prepreg with a 70 wt% resin portion.

[0059]

A 12 μ m-thick electrolytic copper foil (trade name: F2-WS-12 by Furukawa Electric Co., Ltd.) was stacked onto both sides of the prepreg with the adhesive sides facing the prepreg, and subjected to pressing conditions of 230°C, 90 min, 4.0 MPa to fabricate a double-sided copper clad laminate. The fabricated double-sided copper clad laminate was used for the following evaluation.

[0060]

(Evaluations)

(1) The copper foil peel strength of the double-sided copper clad laminate was measured.

(2) The time until abnormalities such as swelling or peeling appeared after immersion in soldering baths at 260°C and 288°C was measured.

(3) The copper foil was etched for removal and the laminate was folded to evaluate the pliability. ○: No fracture, × Fracture.

(4) The laminate with the copper foil removed on one side by etching was subjected to moisture absorption treatment for one hour with PCT saturation conditions of 121°C, 2 atmospheres, and then immersed for 20 seconds in a soldering bath at 260°C, upon which abnormalities such as swelling or peeling of the laminate were observed (PCT resistance). ○: No abnormalities, × Abnormalities.

The obtained results are shown in Table 1.

[0061]

[Table 1]

Evaluation	Units	Example 1	Example 2	Example 3	Comparative Example 1
PAI	-	Synthesis Example 1	Synthesis Example 2	Synthesis Example 3	KS6600
PAI/Ep	pts. by wt.	80/20	80/20	80/20	80/20
Pliability	-	○	○	○	×
260°C soldering	sec.	>300	>300	>300	150
288°C soldering	sec.	>300	>300	>300	60
PCT resistance	-	○	○	○	×
Copper foil peel strength	kN/m	1.0	0.8	0.9	0.6

[0062]

All of the prepreps of Examples 1-3 containing polyamideimide resins with structures according to general formula (1) were satisfactory with high values of 0.8-1.0 kN/m for the copper foil peel strength. Also, the soldering heat resistance (260°C soldering, 288°C soldering) was 5 minutes or longer at both temperatures, and no abnormalities such as swelling or peeling were observed. Also, the pliability was sufficient

to allow folding of the laminate as desired. Moreover, no abnormalities such as swelling or peeling were observed in the soldering bath immersion at 260°C for 20 seconds when moisture absorption treatment was carried out under PCT saturation conditions of 121°C, 2 atmospheres.

[0063]

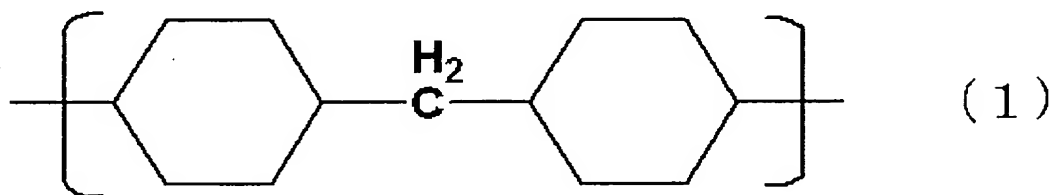
In contrast, the prepreg or metal foil-clad laminate of Comparative Example 1 had a low copper foil peel strength of 0.6 kN/m. Furthermore, the pliability was poor and fracturing occurred when the laminate was folded. In addition, the soldering heat resistance and PCT resistance were inferior, and abnormalities such as swelling and peeling were observed.

[Document Name] Abstract

[Abstract]

[Problem] The present invention provide a printed circuit board with excellent adhesion property, dimensional stability and heat resistance and the ability to be bent and housed at high density in electronic device packages, as well as to provide a prepreg and metal foil-clad laminate which yield said printed circuit board.

[Means of Solution] A prepreg obtained by impregnating a resin composition comprising a resin having a structure represented by the following general formula (1) into a fiber base material.



[Selected Drawing] None